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(22) Filing Date: July 5, 1996	Asahi Chemical Industry Co., Ltd.
	(72) Inventor: Takahiko Kondo
	(72) Inventor: Takuya Hasegawa
	(74) Agent: Takeshi Shimizu, Patent Attorney (and two others)

(54) [ Title of the Invention ] **Microporous Polyethylene Membrane**

(57) [ Abstract ]

[ Object ] To provide a microporous polyethylene membrane that has better workability and results in better productivity, and that has high heat resistance capable of ensuring greater battery safety under stringent conditions.

[ Means ] A more heat-resistant microporous polyethylene membrane having a strain-hardening elongation viscosity, a gel fraction of less than 1%, and an average pore diameter of 0.001 to 0.1  $\mu\text{m}$ ; a battery separator using it; and a battery using the battery separator.

[ Merit ]        The better workability and productivity, and the higher heat resistance of the membrane allow more reliable batteries to be produced when it is used as battery separator.

[ Claims ]

[ Claim 1 ] A more heat-resistant microporous polyethylene membrane, characterized by having a strain-hardening elongation viscosity, a gel fraction of less than 1%, and an average pore diameter of 0.001 to 0.1  $\mu\text{m}$ .

[ Claim 2 ] A battery separator featuring the use of a microporous polyethylene membrane according to Claim 1.

[ Claim 3 ] A battery featuring the use of a battery separator according to Claim 2.

[ Detailed Description of the Invention ]

[ 0001 ]

[ Technical Field to Which the Invention Belongs ]

The present invention relates to a microporous polyethylene membrane suitable for use as a battery separator.

[ 0002 ]

[ Prior Art ]

Progress has recently been made in increasing the capacity of batteries, such as lithium ion batteries. As a result, an increasingly important issue has become battery safety during malfunctions such as short circuits. Microporous polyethylene membranes have been used as separators in such high capacity batteries, particularly lithium ion batteries. Such microporous polyethylene membranes are used because of their general properties, such as their mechanical strength and permeability, as well as their ability to develop the "Fuse Effect," where the separator melts to form a film covering the electrodes and cuts off the current when the battery internally overheats, thereby ensuring battery safety.

[ 0003 ]

Microporous polyethylene membranes are known to have a fuse temperature, which is the temperature at which the fuse effect takes place, of around 130 to 150°C. If for some reason the battery internally overheats, the current is shut down and the battery reaction is stopped when the fuse temperature is reached. However, the fuse effect can sometimes fail to take place in time when the temperature increases rapidly or the like. That is because the separator stretches and becomes broken due to the contracting force that is produced when the separator melts or due to the pressure persisting between the electrodes after the melt down, resulting in shorts between the positive and negative electrodes. Cross linked microporous polyethylene membranes have

been used recently to endow separators with better heat resistance capable of ensuring battery safety even under more stringent conditions such as the above.

[ 0004 ]

Problems, however, with all conventional methods for cross linking microporous polyolefin membranes are that the gel content complicates processes such as stretching, the production efficiency is compromised, and so forth. Japanese Unexamined Patent Application (Kokai) 1-167344, for example, discloses a method for cross linking microporous polyolefin membranes with cross linkers, but the microporous polyolefin membrane obtained by this method contains an abundance of gel, complicating the stretching process and the like, and does not give a membrane with high strength.

[ 0005 ]

Japanese Unexamined Patent Application (Kokai) 56-73856 discloses a method for cross linking microporous polyolefin membranes by means of ionizing radiation, but the microporous polyolefin membrane obtained by this method also contains gel. Other problems are the need for a high energy process, which causes the polyolefin to heat up while irradiated, so that the microporous membrane sometimes melts or shrinks. A necessary remedy is to separately carry out a number of treatments with lower energy.

[ 0006 ]

[ Problems Which the Invention Is Intended to Solve ]

An object of the invention is to provide a microporous polyethylene membrane that has better workability and results in better productivity, and that has high heat resistance capable of ensuring greater battery safety under stringent conditions.

[ 0007 ]

[ Means for Solving the Abovementioned Problems ]

As a result of extensive research undertaken to address the objects of the invention, the present invention was perfected upon the discovery that microporous polyethylene membranes characterized by specific thermal deformation behavior had higher heat resistance, with a gel fraction of less than 1%, resulting in better workability and productivity, as compared to microporous membranes lacking such behavior. That is, the first of the inventions is a microporous polyethylene membrane, characterized by strain-hardening during the measurement of elongation viscosity, and a gel fraction of less than 1%, preferably with an average pore

diameter of 0.001 to 0.1  $\mu\text{m}$ , as determined by a permeability method. The second of the inventions is a battery separator featuring the use of such a microporous polyethylene membrane. The third of the inventions is a battery featuring the use of such a battery separator.

[ 0008 ]

The invention is described in detail below. The microporous polyethylene membrane of the invention is described first. Although it is not clearly understood why the microporous polyethylene membrane with strain-hardening properties and a gel fraction of less than 1% has high heat resistance, the heat resistance as determined in overcharging tests and breaking tests at elevated temperature, for example, can be dramatically improved in comparison to ordinary microporous polyethylene membranes lacking such strain-hardening properties. The method for endowing membranes with such strain-hardening properties is simple and does not compromise the workability or productivity of conventional membranes.

[ 0009 ]

The elongation viscosity is a physical constant with a considerable effect on melt tension during extension and deformation. It can be readily determined with a commercially available elongation viscosity meter (such as the Melten Rheometer by Toyo Seiki), and is normally expressed as a function of strain rate and time. As illustrated in Figure 2, the elongation viscosity of a molten microporous polyethylene membrane which normally contains no gel increases, when stretched at a constant strain rate from a relatively fixed point, until it is dependent on the strain rate, and then tends to decrease precipitously as it approaches breakage. This type of breakage is referred to as ductile fracture.

[ 0010 ]

As illustrated in Figure 1, on the other hand, the elongation viscosity of the molten microporous polyethylene membrane of the invention increases longer than the normal type when stretched under the same conditions, tending to increase at a linear or greater rate near the breaking point until sudden breakage. This type of breakage is referred to as elastic break. These properties indicate strain-hardening properties. Details on elongation viscosity can be found, for example, in Kiyohito Koyama, *Journal of the Japanese Society of Rheology*, **19**, 174 (1991). The gel fraction is determined based on ASTM D2765. The gel fraction in the invention is less than 1%. A gel fraction of 1% or more makes processes such as stretching more difficult and lowers productivity.

[ 0011 ]

The heat resistance of a separator made of the microporous membrane of the invention is comprehensively evaluated in accelerated tests involving heating tests as well as external short and overcharging tests on batteries assembled using the separator. As a result of detailed study of the breaking behavior of the membrane after melting, the inventors found that the results of the accelerated tests were strongly correlated to the break time in silicon oil at 160°C.

[ 0012 ]

That is, the microporous polyethylene membrane of the invention has a break time of at least 20 seconds in 160°C silicon oil. Such membranes passed all of the above accelerated tests. Conventional microporous polyethylene membranes, on the other hand, all failed one or more of the accelerated tests, with a break time of 20 seconds or less, which was consistent with the results of the accelerated tests. That is, a characteristic feature of the microporous polyethylene membrane of the invention is the break time in 160°C silicon oil.

[ 0013 ]

The microporous polyethylene membrane of the invention thus has high heat resistance, but with an air permeability of no more than 2000 seconds, as determined on the basis of 25  $\mu$ , and a breaking strength of at least 500 kg/cm<sup>2</sup>, resulting in far better heat resistance as well as mechanical strength and permeability than conventional microporous polyethylene membranes. The polyethylene used in the invention should be high density polyethylene, which is a crystalline polymer based on ethylene. Blends with no more than 30% polyolefin, such as polypropylene, medium density polyethylene, linear low density polyethylene, low density polyethylene, and EPR may also be used.

[ 0014 ]

The weight average molecular weight of the polyethylene should be 100,000 to 4,000,000, preferably 200,000 to 1,000,000, and even more preferably 200,000 to 700,000. A molecular weight under 100,000 tends to result in breakage during stretching, while more than 4,000,000 will complicate the manufacture of hot solution. The weight average molecular weight may be adjusted to within the desired range by blending polyethylenes of different molecular weight, by multiple stage polymerization, or the like. The membrane should be 1 to 200  $\mu$ m thick, and preferably 10 to 50  $\mu$ m thick. Less than 1  $\mu$ m will result in unsatisfactory mechanical

strength, while more than 200  $\mu\text{m}$  will cause problems when attempting to make lighter, more compact batteries.

[ 0015 ]

The air permeability should be 20 to 80%, and preferably 30 to 60%. Less than 20% will result in poor permeability, while more than 80% will not result in satisfactory mechanical strength. The mean pore diameter should be 0.001 to 0.1  $\mu\text{m}$ , preferably 0.005 to 0.5  $\mu\text{m}$ , and even more preferably 0.01 to 0.03  $\mu\text{m}$ . A mean pore diameter under 0.001  $\mu\text{m}$  will result in poor permeability, while more than 0.1  $\mu\text{m}$  will slow down the interruption of the current through the fuse effect, with a risk of short circuits caused by deteriorating electrolyte or precipitated dendrites.

[ 0016 ]

A method for producing the microporous polyethylene membrane of the invention is described below. The method comprises the following three steps of forming the membrane, stretching it, and extracting it.

#### Forming the Membrane

A polymer gel, which is an intermediate in the invention, is produced by dissolving polyethylene in a plasticizer at or over the melting point to produce a hot solution which is then cooled to no more than the crystallization temperature. The plasticizer referred to here is an organic compound capable of forming a homogenous solution with polyethylene at a temperature no greater than the boiling point. Specific examples include decalin, xylene, dioctyl phthalate, dibutyl phthalate, stearyl alcohol, oleyl alcohol, decyl alcohol, nonyl alcohol, diphenyl ether, n-decane, n-dodecane, and paraffin oil, paraffin oil and dioctyl phthalate are preferred. The proportion of plasticizer is not particularly limited, but is preferably 20% to 90%, and more preferably 50% to 70%. Less than 20% will interfere with achieving a suitable porosity, while more than 90% will result in a lower viscosity which will complicate continuous formation.

[ 0017 ]

The polymer gel is formed into a sheet with a thickness in the tens of  $\mu\text{m}$  to tens of mm. This is the starting sheet, and the step for producing it is referred to as the membrane-forming step. The method for forming the membrane is not particularly limited. An example is to feed the plasticizer and high density polyethylene powder to an extruder where the ingredients are melt

kneaded at about 200°C, and to then cast the mixture from a common coat-hanger die onto a cooling roll, thereby continuously forming membranes.

[ 0018 ]        Stretching Step

The starting sheet is then stretched at least uniaxially to produce an oriented membrane. The stretching method is not particularly limited. Tenters, rolls, calendaring, and the like can be used. Biaxial stretching with tenters is preferred. The stretching temperature can range from ambient temperature to the melting point of the polymer gel, preferably from 80 to 130°C, and even more preferably from 100 to 125°C. The draw ratio should be 4 to 400-fold, preferably 8 to 200-fold, and even more preferably 16 to 100-fold, based on area. A draw ratio of less than 4-fold will not produce satisfactory separator strength, while more than 400-fold will make stretching difficult and will result in a lower porosity, etc.

[ 0019 ]        Extraction Step

The plasticizer is then extracted from the drawn membrane to produce a microporous membrane. The extraction method is not particularly limited. When paraffin oil or dioctyl phthalate are used, they can be extracted with an organic solvent such as methylene chloride or methyl ethyl ketone (MEK), and then removed when heated and dried at a temperature no greater than the fuse temperature. When a low boiling compound such as decalin is used as the plasticizer, it can be removed by being heated and dried at a temperature no greater than the fuse temperature. In either case, the membrane should be restrained to prevent adverse effects on physical properties caused by membrane shrinkage. To endow the membrane with strain-hardening properties, a treatment with an organic peroxide should be performed during the membrane-forming step, or treatment with ionizing radiation should be performed after any step.

[ 0020 ]        Treatment With Organic Peroxide

A certain amount of an organic peroxide is added to the polyethylene or plasticizer, the ingredients are melt kneaded to produce a hot solution at conditions under which the peroxide does not substantially decompose, the hot solution is heated to the temperature at which the organic peroxide decomposes, and it is cooled to at least the polyethylene crystallization temperature, resulting in a peroxide-treated starting sheet. A microporous polyethylene membrane with strain-hardening properties can be produced through the stretching and extraction steps.

[ 0021 ]



The expression "peroxide does not substantially decompose" means that the active oxygen of the peroxide does not fall below  $\frac{1}{2}$  during the time until a homogenous hot solution is prepared from the polyethylene, plasticizer, and organic peroxide. For example, if it takes 10 minutes to melt knead the ingredients, they should be melt kneaded at a temperature no greater than one resulting in a peroxide half life of 10 minutes, so that a homogenous hot solution can be prepared without the peroxide substantially decomposing. The half life is the time in which the amount of active oxygen reaches falls to  $\frac{1}{2}$  when a benzene solution of 0.1 mol/L organic peroxide is allowed to decompose at a given temperature.

[ 0022 ]

The organic peroxides referred to here are peroxy ketals, dialkyl peroxides, peroxy esters, and the like with a half life of 1 minute or more at 150°C. Examples include  $\alpha, \alpha'$ -bis (t-butylperoxy)diisopropyl benzene, dicumyl peroxide, 2,5-dimethyl-2,5-bis (t-butylperoxy)hexane, t-butyl cumyl peroxide, di-t-butyl peroxide, and 2,5-dimethyl-2,5-bis (t-butylperoxy)hexane-3. The proportion of the organic peroxide is not particularly limited, but is preferably 0.001% to 1%, and more preferably 0.01% to 0.5%. Less than 0.001% will result in unsatisfactory heat resistance, while more than 1% will result in insoluble gel components in the plasticizer, making it difficult to process the solution into a uniform membrane.

[ 0023 ]

Polyfunctional monomer may be added in a proportion no greater than 1%. Examples of polyfunctional monomers include divinyl benzene, diallyl phthalate, triallyl cyanurate, and triallyl isocyanurate. For example, a plasticizer in which the organic peroxide has been dissolved and high density polyethylene powder can be fed to an extruder, they can be melt kneaded at a temperature at or over the polyethylene melting point but no greater than one resulting in an organic peroxide half life of 10 minutes, and the hot solution can be cast onto a cooling roll from a common coat-hanger die heated to at least a temperature at which the organic peroxide half life will be 10 seconds, so as to continuously form membranes.

[ 0024 ]      Electron Beam Treatment

The material can be endowed with strain-hardening properties by ionizing radiation treatment after any of the steps in the method for producing conventional microporous polyethylene membranes noted above. Treatment after extraction by ion beam treatment is preferred. The radiation during ion beam treatment should be 0.1 to 10 Mrad, and preferably 1 to

5 Mrad. Too little radiation will not improve the heat resistance enough, while too much will cause the microporous polyethylene membrane to be heated by the ion beam energy, so that the membrane sometimes melts or shrinks. The strain-hardening properties can thus be readily provided without significantly affecting normal manufacture and productivity.

[ 0025 ]

#### [ Embodiments of the Invention ]

Embodiments of the invention are described in detail below. The following tests were conducted in the examples.

##### 1) Membrane Thickness

Measured using a dial gage (Peacock No. 25 by Ozaki Seisakusho).

##### 2) Porosity

This was determined by the following equation from the volume and weight of 20 cm square samples.

$$\text{Porosity (\%)} = \{ \text{volume (cm}^3\text{)} - \text{weight (g)}/0.95\} / \text{volume (cm}^3\text{)} \times 100$$

##### [ 0026 ] 3) Mean Pore Diameter

When an aqueous solution of 0.05 wt% pullulan (by Showa Denko) was circulated at a differential pressure of 0.5 kg/cm<sup>2</sup>, the concentration of pullulan contained in the filtrate was determined from the differential refractive index. The mean pore diameter (μm) was calculated using the following equation from the molecular weight M of pullulan at 50% inhibition and the intrinsic viscosity {η} of the same aqueous solution.

$$[\eta] M = 2.1 \times 10^{-4} \left( (d/2)^2 \right)^{0.75}$$

##### 4) Gel Fraction

This was determined by the following equation as the ratio of the post-extraction residual mass relative to sample mass prior to extraction based on the change in weight upon the extraction of components solubilized after 12 hours in boiling para-xylene based on ASTM D2765.

$$\text{Gel fraction (\%)} = \text{residual mass (g)} / \text{sample mass (g)} \times 100$$

##### [ 0027 ] 5) Puncture Strength

A puncture test was conducted at a puncture speed of 2 mm/sec with a needle tip radius of 0.5 mm using a KES-G5 Handy Compression Tester by Kato Tech. The greatest puncture load

was considered the puncture strength (g). The puncture strength was multiplied by the membrane thickness ( $\mu\text{m}$ )/25 ( $\mu\text{m}$ ) to calculate the puncture strength in terms of 25  $\mu$ .

#### 6) Air Permeability

This was determined with a Gurley air permeability meter based on JIS P-8117. The air permeability was multiplied by membrane thickness ( $\mu\text{m}$ )/25 ( $\mu\text{m}$ ) to calculate the air permeability in terms of 25  $\mu$ .

#### [ 0028 ] 7) Elongation Viscosity

The microporous membranes were dipped in 150°C silicon oil to relax the orientation, and the elongation viscosity was determined at a strain rate of 0.1/sec using a melt elongation flow measuring device (Melten Rheometer by Toyo Seiki). The presence or absence of strain-hardening properties was determined by the type of breakage. For example, stretching a conventional microporous polyethylene membrane results in neck-in about midway through in the sample, with a precipitous decrease in the elongation viscosity at a certain time before breakage (ductile fracture), whereas the elongation viscosity of microporous polyethylene membranes endowed with strain-hardening properties increases continuously until breakage (elastic break).

#### 8) Membrane Break Test

A microporous polyethylene membrane was secured between two stainless steel washers with an outside diameter of 25 mm, this was held down at four peripheral points by clips, and it was dipped in 160°C silicon oil (KF-96-10CS, by Shin-Etsu Kagaku). Membranes which broke within 20 seconds, as determined by macroscopic assessment, were rated  $\times$ , those which did not break were rated O.

#### [ 0029 ] 9) Overcharging Test

Lithium ion batteries were produced using  $\text{LiCoO}_2$  as the positive electrode active material, graphite and acetylene black as the conductor, and fluorine rubber as the adhesive, resulting in an 88:7.5:2.5:2 weight ratio mixture of  $\text{LiCoO}_2$ :graphite:acetylene black:fluorine rubber, which was applied in the form of a dimethyl formamide paste onto aluminum foil and dried. The resulting sheet was used as the positive electrode. A 95:5 weight ratio mixture of needle coke and fluorine rubber was applied in the form of a dimethyl formamide paste onto copper foil and dried. The resulting sheet was used as the negative electrode. Lithium borofluoride was adjusted to a concentration of 1.0 M in a propylene carbonate and butyrolactone

solvent mixture (volumetric ratio = 1:1) as the electrolyte. The batteries were charged for 5 hours at 4.2 V, and were then overcharged at a constant current. The overcharging caused the interior of the batteries to heat up. The current was shut down when the fuse temperature was reached. Samples in which no current was restored 1 hour or later were rated O. Because these were accelerated tests, they were conducted without any of the safety features such as PTC elements which are normally set up in actual batteries.

[ 0030 ]      Example 1

40 parts high density polyethylene with a weight average molecular weight of 250,000, 60 parts paraffin oil (P350P by Matsumura Petroleum), and 0.2 part dicumyl peroxide (150°C half life about 10 min, 200°C half life about 7 sec) were kneaded for 5 min at 150°C and 50 rpm in a batch type melt kneader (Labo Plastomill by Toyo Seiki). The resulting kneaded mixture was molded with a 200°C heated press, heated as such for 10 minutes, and then cooled with a water-cooled press, giving a 1000  $\mu$ m thick starting sheet. This was drawn at 120°C to a factor of 6  $\times$  6 using a simultaneous biaxial stretching machine (by Toyo Seiki), and the paraffin oil was then extracted with methylene chloride. The properties of the resulting microporous polyethylene membrane are given in Table 1.

[ 0031 ]      Example 2

A microporous polyethylene membrane was produced in the same manner as in Example 1 except that 0.8 part dicumyl peroxide was used. The properties of the resulting microporous polyethylene membrane are given in Table 1.

Comparative Example 1

A microporous polyethylene membrane was produced in the same manner as in Example 1 except that no organic peroxide was added. The properties of the resulting microporous polyethylene membrane are given in Table 1.

Comparative Example 2

An attempt was made to produce a microporous polyethylene membrane in the same manner as in Example 1 except that 6 parts organic peroxide was added, but considerable stretching stress caused the membrane to break, and the membrane could not be processed to the required draw ratio.

[ 0032 ]

[ Table 1 ]

	Example 1	Example 2	Comp. Ex. 1	Comp. Ex. 2
membrane thickness ( $\mu\text{m}$ )	25	28	24	--
porosity (%)	40	38	45	--
pore diameter ( $\mu\text{m}$ )	0.03	0.02	0.04	--
puncture strength (g/25 $\mu$ )	400	450	300	--
air permeability (sec/25 $\mu$ )	620	710	470	--
gel fraction (%)	0	0	0	20
strain-hardening	yes	yes	no	--
break test (160°C)	O	O	x	--

[ 0033 ]      Example 3

40 parts high density polyethylene with a weight average molecular weight of 250,000, 60 parts paraffin oil (P350P by Matsumura Petroleum), and 0.4 part dicumyl peroxide were kneaded at 150°C in a 35 mm biaxial extruder, and the kneaded mixture was cast from a 200°C coat-hanger die (1400  $\mu\text{m}$  lip interval) onto a cooling roll adjusted to 30°C to produce a 1400  $\mu\text{m}$  thick starting sheet. The sheet was stretched at 120°C to a factor of  $7 \times 7$  using a simultaneous biaxial stretching machine, and the paraffin oil was then extracted with methylene chloride. The properties of the resulting microporous polyethylene membrane are given in Table 2.

[ 0034 ]      Example 4

40 parts high density polyethylene with a weight average molecular weight of 250,000 and 60 parts paraffin oil (P350P by Matsumura Petroleum) were kneaded at 200°C in a 35 mm biaxial extruder, and the kneaded mixture was cast from a coat-hanger die (1400  $\mu\text{m}$  lip interval) onto a cooling roll adjusted to 30°C to produce a 1400  $\mu\text{m}$  thick starting sheet. The sheet was stretched to a factor of  $7 \times 7$  using a simultaneous biaxial stretching machine, and the paraffin oil was then extracted with methylene chloride. The extracted membrane was irradiated with a 3 Mrad ion beam in a nitrogen atmosphere with an oxygen concentration of 50 ppm. The accelerated voltage was 150 kV. The properties of the resulting microporous polyethylene membrane are given in Table 2.

Comparative Example 3

A microporous polyethylene membrane was obtained in the same manner as in Example 2 except that no organic peroxide was added. The properties of the resulting microporous polyethylene membrane are given in Table 2.

[ 0035 ]

[ Table 2 ]

	Example 3	Example 4	Comp. Ex. 3
membrane thickness ( $\mu\text{m}$ )	23	29	29
porosity (%)	37	48	40
pore diameter ( $\mu\text{m}$ )	0.02	0.04	0.04
puncture strength (g/25 $\mu$ )	600	550	620
air permeability (sec/25 $\mu$ )	750	450	470
gel fraction (%)	0	0	0
strain-hardening	yes	yes	no
break test (160°C)	O	O	x
overcharge test 2A	O	O	break
3A	O	O	break

[ 0036 ]

[ Merit of the Invention ]

Because the microporous polyethylene membrane of the invention has high heat resistance, its use as a battery cell separator in particular results in better safety in terms of the fuse effect, with no restoration of current due to membrane breakage. This allows safer batteries to be provided.

[ Brief Description of the Figures ]

Figure 1 illustrates the relationship between time (sec) and elongation viscosity (poise) in the microporous polyethylene membranes having strain-hardening properties in Examples 1 and 2. Figure 2 illustrates the relationship between time and elongation viscosity in the microporous polyethylene membrane lacking strain-hardening properties in Comparative Example 1.

Figure 1

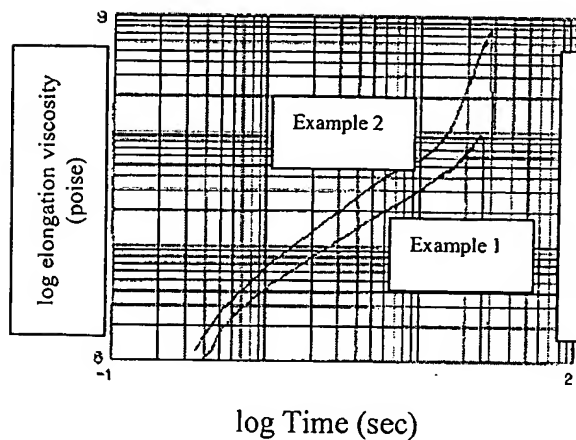
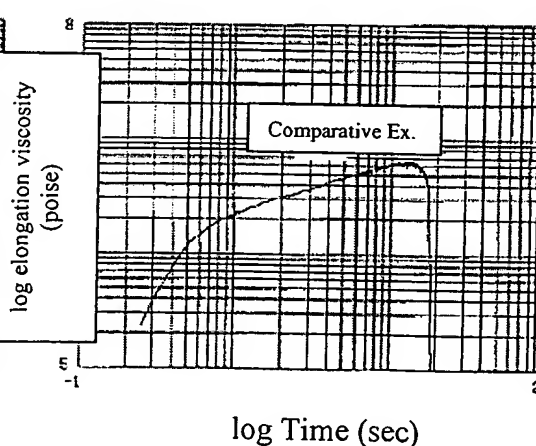


Figure 2



[Amendments to the original Japanese text have been incorporated in the translation.]